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Decolorization of Methyl Orange Using Mill Scale by Photo-Fenton Reaction

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Abstract

The textile dyeing industries generate large amount of effluents, sewage sludge and solid waste materials everyday which are being directly discharged into the surrounding channel, agricultural fields, irrigation channels, surface water and these finally enter into river. The presence of dyes in surface and subsurface water is making them not only aesthetically objectionable but also causes many water borne diseases. Various options have been being employed to treat such wastes. These include chemical treatment such as chlorination and ozonation, electrochemical treatment, physical treatment such as adsorption by activated carbon and membranes, biological treatment and advanced oxidation processes (AOPs). AOPs have attracted wide interests in wastewater treatment. AOPs are based on the generation of hydroxyl radicals in water, which are highly reactive and next on Selective oxidants being able to oxidize organic compounds particularly unsaturated organic compounds such as azo dyes. Among AOPs, two of the most important processes to generate hydroxyl radicals are using the photo-Fenton and photo-ferioxalate ($Fe^{2+}/H_2O_2/UV$ and $Fe^{2+}/OA/UV$) systems. In the present study, the aqueous solution of Methyl Orange (MO), a model organic dye has been subjected to photocatalytic degradation by UV irradiation in presence of mill scale (iron oxide, solid waste generated in steel plants) containing different concentrations of H_2O_2 employing photo-Fenton process. The effect of various parameters such as initial mill scale amount, initial hydrogen peroxide (H_2O_2) concentration & initial dye concentration on decolorization process has been studied. The experiments were carried out by varying amount of mill scale (0.01-0.3 g/100 mL), initial concentration of dye (0.01-0.10 mM/100 mL) and hydrogen peroxide concentration (1-4 mL/100 mL). The optimum mill scale content was found to be 50 mg/100 mL. The degradation rate decreased with increasing dye concentration.

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Keywords: Photo-fenton, Photocatalytic degradation, Methyl Orange.

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1. Introduction

Water pollution i.e. the pollution of water bodies on the planet, is one of the raging environmental issues that our planet is facing today. It occurs when pollutants (e.g. untreated dyes in effluents from dyeing factories and leather industries) are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. From pollution point of view, dyeing, leather, sugar, pulp and paper industries are the major contributors. Due to the complex aromatic structure and stability of these dyes, conventional biological pre-treatment methods are ineffective for degradation. A number of physical and chemical techniques had been reported for the treatment of dye effluent over the past few years. In most cases, the degradation is conducted for dissolved compounds in water with UV radiation. Recently, advanced oxidation processes (AOPs) have been found to be very effective for removing organic pollutants from wastewater [1, 2]. The AOPs involve the generation of hydroxyl radicals ($HO^{\bullet}$) which can degrade most organic compounds to carbon dioxide and water due to their high oxidation potential (E_0 = +2.80 V) [3]. The use of semiconducting materials like iron oxide as a photocatalyst for various chemical reactions are well received due to their unique optoelectronic and photocatalytic properties. For the decomposition of dyes, mill scale with H_2O_2 under UV is considered due to its stability as a support in solution. Among AOPs, two of the most important processes to generate hydroxyl radicals are using the Fenton and photo-Fenton (Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2/UV) systems [4]. In these reactions, H_2O_2 is added as the direct source of $HO^{\bullet}$ [5, 6].

The use of Fe^{2+}/H_2O_2 as an oxidant for wastewater treatment is attractive since iron is highly abundant and non-toxic, and a 30% H_2O_2 aqueous solution is easy to handle and environmentally not harmful.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (1)$$

In the dark, the reaction is retarded after complete conversion of Fe^{2+} to Fe^{3+}. Thus Organic pollutant degradation rate could be increased by irradiation of Fenton with UV light (Photo - Fenton process). UV light leads not only to the formation of additional hydroxyl radicals but also to the recycling of ferrous catalyst by reduction of Fe^{3+}. In this way, the concentration of Fe^{2+} is increased and the overall reaction is accelerated. It is reported that the removal rate is strongly dependent on the initial concentration of the dye, Fe^{2+} and H_2O_2 [7].

The UV/H_2O_2 process involves the photolysis of hydrogen peroxide. The most accepted mechanism for this H_2O_2 photolysis is the rupture of the O-O bond by the action of ultraviolet light forming two hydroxyl radicals.

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \quad (2)$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (\lambda<400 \text{ nm}) \quad (3)$$

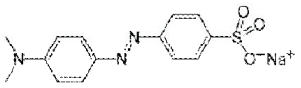
In the present study MO is used as model organic pollutant and its degradation is studied in the presence of mill scale obtained from local steel plant in H_2O_2 solution under UV light.

2. Experimental Details:

2.1. Material

Main reagents were MO, H_2O_2 and mill scale. Mill scale was collected from local steel plant. All other chemicals with analytical grade were purchased. All the chemicals were used without further purification to decompose the dye. Properties of MO are shown in Table 1.

Table 1. roperties of Methyl Orange

Name	Methyl Orange
Wavelength λ_{max} (nm)	463
Molecular weight (g/mol)	327.334029
Molecular structure	

2.2. Procedure

The photo degradation of MO was carried out using two 8W black light lamps with the main emission at 365nm. The sample suspension was formed by adding varying amounts of mill scale to 100 ml of aqueous solution containing MO and H_2O_2. Before photoreaction, the suspension was magnetically stirred in the dark for 30 minute to establish an adsorption-desorption equilibrium. The aqueous suspensions were then illuminated by UV while being magnetically stirred. At the specific time intervals, the analytical samples were withdrawn from the suspension and then stored in the dark for needed analysis. The absorbance spectrum in each experiment was determined from a UV-vis spectrophotometer and the degradation of MO was monitored by recording the absorbance at λ=463 nm as a function of illumination time.

3. Results and Discussion

3.1. Effect of combinations of Mill scale, H_2O_2 and UV

A set of experiments were carried out under different conditions through MO alone, MO + UV, MO + Mill Scale, MO + H_2O_2, MO + Mill Scale+ H_2O_2, MO + UV+ Mill Scale, MO + UV+ H_2O_2, MO + UV+ Mill Scale+ H_2O_2. Figure 1 shows percentage of photodecomposition of MO under these experimental conditions. Solution containing only H_2O_2 shows almost no decomposition of MO after 60 min reaction. UV illumination with H_2O_2 but no mill scale also shows very slight decomposition after 60 min reaction. But combination of mill scale, H_2O_2 and UV shows very fast decomposition (>90% after 60 min).

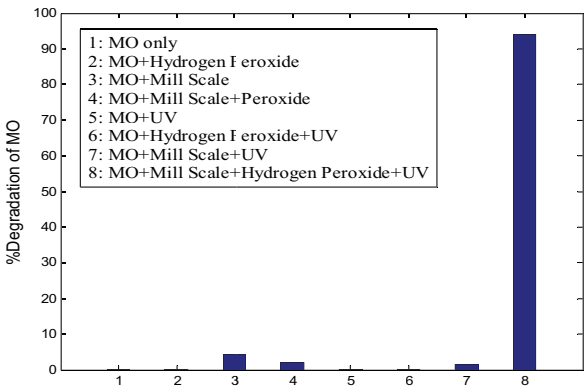


Fig.1. Effect of combinations of Mill Scale, H_2O_2 and UV

This is because hydrogen peroxide and UV together, form two free hydroxyl radicals (HO•) which are potent oxidizing agents.

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet}$$

The free hydroxyl radicals are excited state species since they are characterized by one-electron deficiency and are therefore extremely unstable. Because of their instability, they tend to react with the first chemical it comes in contact with Hydroxyl radicals ($HO^{\bullet}$) also tend to completely oxidize dissolved organic contaminants in aqueous media and produce carbon dioxide, water and salts as by products. Hydrogen peroxide is catalyzed with UV irradiation to create highly reactive radicals which react rapidly. Therefore the combination results fastest decomposition of MO. The necessity of using this combination is also reported earlier [8]

3.2. Effect of Mill scale concentration in MO decomposition

Equations and formulae Mill scale produces hydroxyl radical which is primary requirement to break the bond of the MO. So we may expect that more amount of mill scale will produce hydroxyl radical as well as the MO degradation. But in practical we found it to be different and got an optimum value. To measure this optimum value a set of experiments were carried out by varying the amount of mill scale from 0.01 g to 0.3 g in 100 ml 0.1 mM MO decomposition.

From the result (shows in figure 2) it is clearly seen that the decomposition of MO is distinctly increased with the increasing amount of mill scale up to 50mg/L. The lesser decomposition capacity of Fe2+ at lower concentration might be attributed due to the less hydroxyl radical production [9] which increases with increasing amount of catalyst from 10mg/L to 50mg/L. This is because more $HO^{\bullet}$ radicals are produced with the increase of Fe2+ according to Equation below [10, 11, 12].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$$

With increasing the mill scale amount above 0.05g/L, the decomposition rate again slows down which is clearly shown in Figure 3. This is because excess of Fe^{2+} ions, produced by the photo reduction of Fe^{3+} ions in the solution, compete for the hydroxyl radicals along with the dye molecules and act as hydroxyl radical scavenger [13, 14, 15, 16].

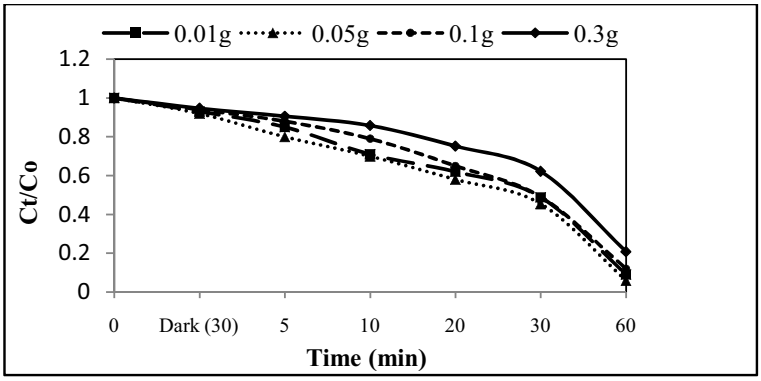


Fig. 2. Effect of mill scale concentration on MO decomposition. Experimental conditions: [MO] = 0.1mM; H_2O_2 = 2 ml/100 ml; reaction time = 60 min.

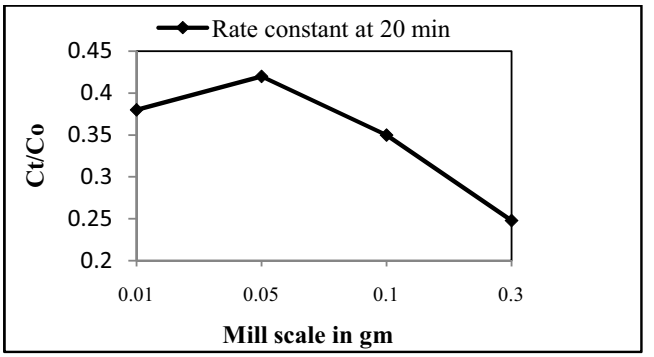


Fig. 3. Rate constant curve showing effect of mill scale concentration on MO decomposition. Experimental conditions: [MO] = 0.1 mM; H_2O_2 = 2 ml/100 ml; reaction time = 20 min.

Fe^{2+} also has a catalytic decomposition effect on H_2O_2. When Fe^{2+} concentration is increased, the catalytic effect also increases accordingly and when its concentration was higher, a great amount of Fe^{3+} was produced.

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^{-}$$

Moreover, Fe^{3+} ion could react with H_2O_2 to form hydroperoxyl radicals which is significantly less oxidizing agent than $HO^{\bullet}$ [17].

In addition decomposition occurs in the suspension of mill scale in MO solution since mill scale is not soluble in water. So penetration of the UV light into the sample is highly dependent upon its concentration. At higher concentration, solution becomes opaque and light radiation cannot enter in to activate the catalyst particles. Hence the rate of dye degradation decreases [18].

3.3. Effect of Hydrogen Peroxide concentration in MO decomposition

Another set of experiments were carried with varying the amount of H_2O_2 from 1 ml to 4 ml for 100 ml 0.1 mM MO decomposition It was found (Figure 4) that the rate of decolorization rises by increasing the initial dosage of H_2O_2 up to a 'critical'' value at which it is maximum and beyond which it is inhibited [19, 20, 21]. This phenomenon could be explained by considering the two opposing effects of H_2O_2 in the photo-oxidation reaction, explained as follows:

When increasing quantities of H_2O_2 are added to the solution, the fraction of light absorbed by the photo-decomposition increases, and, consequently, so does its photolysis rate. More hydroxyl radicals are available for dye oxidation [19, 22].

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet}$$

If additional H_2O_2 is used, access H_2O_2 acts as a scavenger of highly reactive OH free radicals to form much less reactive peroxyl radicals which further consume $HO^{\bullet}$ forming oxygen. This can be expressed by the following reactions [22, 23, 24].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$$

$$^{\bullet}OOH + HO^{\bullet} \rightarrow H_2O + O_2$$

In addition, $HO^{\bullet}$ radicals, generated at high local concentration, will readily dimerize to H_2O_2. As a consequence, there should be a favorable hydrogen peroxide concentration for the effective removal of dyes,

corresponding to the maximum color degradation, so an optimum hydrogen peroxide concentration exists. Thus if H_2O_2 concentration is increased above this limiting value, competition for $HO^{\bullet}$ can be anticipated.

These predictions are in good agreement with the experimental data which is clearly observed from rate constant curve shown in figure 5. Here decomposition rate is the fastest for 2 ml H_2O_2

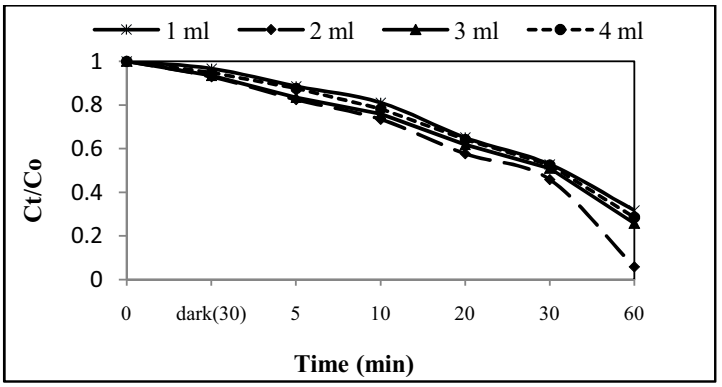


Fig. 4. Effect of H_2O_2 concentration on MO decomposition. Experimental conditions:[MO] = 0.1 mM; Mill scale = 0.05 g/100 ml; reaction time = 60 min

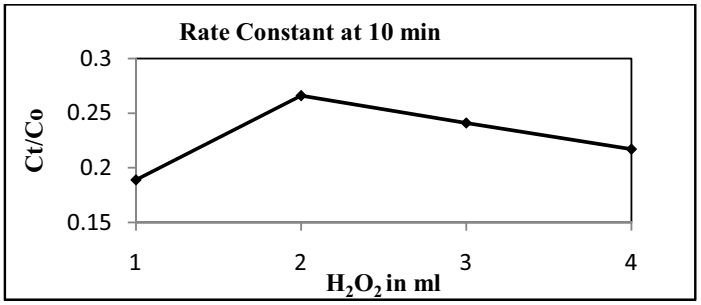


Fig. 5. Rate constant curve showing effect of H_2O_2 concentration on MO decomposition. Experimental conditions: [MO] = 0.1 mM; Mill scale = 0.05 g/100 ml; reaction time = 10 min

3.4. Effect of MO concentration on decomposition rate

A set of experiments were performed by varying MO concentration from 0.01 mM to 0.1 mM. Variation in MO concentration shows that lower the concentration higher the reaction rate although higher concentration can also be decomposed under UV (Figure 6).

An explanation to this behavior is that the higher the initial concentration, the higher the adsorbed organic substances on the surface of the catalyst and the solution became more intensely colored. Therefore, there are only fewer active sites for adsorption of OH^- so the generation of •OH will be reduced. Furthermore, as the concentration of methyl orange increases with constant intensity of UV illumination, the path length of photons entering the solution decreased, so only fewer photons reached the catalyst surface. As a result, the productions of holes or hydroxyl radicals that can attack the pollutants were limited. Therefore, the relative number of •OH attaching the compound decreases and thus the photodegradation efficiency decreases [25].

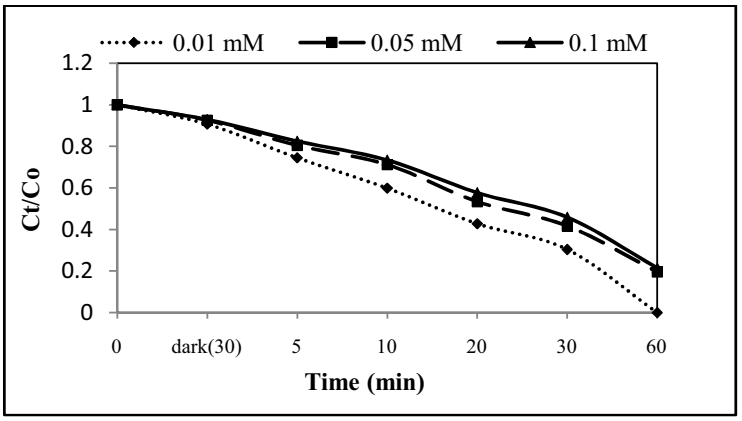


Fig 6: Effect of MO concentration variation on MO decomposition; Experimental conditions: Mill scale = 0.05 g/100 ml; H_2O_2 = 2 ml/100 ml reaction time = 60 min

4. Conclusion

Experimental results indicated that the combination of mill scale, hydrogen peroxide and light illumination is essential for the photodecomposition of MO. The rate of decolorization increased with an increase in mill scale & hydrogen peroxide upto an optimum value beyond which it decreased again. Moreover although any concentration of dye can be decomposed by using optimum amount of other catalysts but reaction rate increases with decreasing dye concentration.

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